

# PATENT SPECIFICATION

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## COMPLETE SPECIFICATION

### Improvements in Recovery of Polycarboxylic Acid Anhydrides

We, CHEMPATENTS, INC., a corporation organized under the laws of the State of Delaware, of 2 Park Avenue, in the City, County and State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

10 This invention relates to the recovery of polycarboxylic acid anhydrides from dilute gaseous mixtures containing them by a cyclic system of scrubbing the anhydride from the gas by means of liquid dibutyl phthalate, stripping the anhydride from the solvent, and then recycling the solvent to the scrubbing step, and more particularly, it relates to such a process wherein the stripping conditions are maintained within critical limits to permit both high capacity and high efficiency operation for a given plant. The invention relates especially to the recovery of phthalic anhydride or maleic anhydride from dilute gaseous mixtures containing them.

25 Polycarboxylic anhydrides such as maleic anhydride and phthalic anhydride have achieved considerable commercial importance. They may be prepared in known manner by the selective partial oxidation of suitable starting materials such as benzene and naphthalene with an oxygen containing gas, using a vanadium oxide catalyst whereby there is produced a gaseous reaction mixture containing up to about 2% by volume of the anhydride together with by-products, inerts, and the like.

35 Dibutyl phthalate has been proposed as a solvent for scrubbing the anhydride from such reaction gases, followed by a series of stripping operations wherein the final stage was maintained at 5—10 mm. mercury pressure. When such a system is attempted on a large scale with a high throughput, it is found that there is insufficient removal of polycarboxylic acid anhydride in the stripping operations, so that 40 when the solvent is recycled to the scrubbing step, the solvent does not efficiently scrub out the polycarboxylic acid anhydride from the gaseous mixture.

The art is confronted with the problem of providing a high throughput, high efficiency 50 polycarboxylic acid anhydride recovery system having the advantages associated with the use of dibutyl phthalate as the scrubbing agent.

It has been found in accordance with the invention that by carrying out the stripping in 55 two steps, each under critically controlled conditions as hereinafter defined, i.e., by scrubbing of the polycarboxylic acid anhydrides from dilute gaseous mixtures containing them with liquid dibutyl phthalate as the scrubbing 60 agent, stripping the absorbed anhydride therefrom under the indicated critical conditions to thoroughly remove the absorbed polycarboxylic acid anhydride, and then recycling the lean solvent to the scrubbing step; the process may be 65 carried out on a large scale with high throughput and high efficiency of operation, giving substantially complete removal of the polycarboxylic acid anhydride from the gaseous mixture and giving a high purity polycarboxylic 70 acid anhydride product.

The invention, therefore, provides a process for the recovery of only maleic anhydride or only phthalic anhydride from a dilute gaseous mixture containing maleic anhydride or 75 phthalic anhydride respectively, or containing a mixture of both of said anhydrides, which comprises scrubbing only the maleic or only the phthalic anhydride vapor from the gaseous mixture with dibutyl phthalate as scrubbing 80 liquor, stripping the absorbed anhydride from the resulting solution comprising only one of said anhydrides at a temperature in the range of 75 to 250° C. and an absolute pressure in the range of 10 to 150 mm. Hg. and then 85 subjecting the partially stripped solution to further stripping under more severe conditions at a temperature in the range of about 75 to 250° C. and an absolute pressure in the range of about 12 to 60 mm. Hg. recycling the 90 anhydride product from the second stripping operation to the first stripping operation and recycling the stripped solvent from the second stripping operation to the anhydride absorption 95 step.

The objects achieved in accordance with the

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invention as described herein include the provision of a commercially advantageous process for recovering phthalic anhydride or maleic anhydride from dilute gaseous mixtures containing either one or both of the anhydrides by scrubbing the gaseous mixture with liquid dibutyl phthalate, thoroughly stripping the absorbed polycarboxylic acid anhydride from the dibutyl phthalate solvent under critically controlled conditions and recycling the dibutyl phthalate to the scrubbing step; the provision of such a process for the recovery of phthalic anhydride from a dilute gaseous mixture containing it; the provision of such a process for the recovery of maleic anhydride from a dilute gaseous mixture containing it; and other objects which will be apparent as details or embodiments of the invention are set forth hereinafter.

In connection with this description, reference is made to the accompanying drawing which sets forth a schematic flow diagram for the process.

In order to facilitate a clear understanding of the invention, the following preferred specific embodiments are described in detail.

#### EXAMPLE 1. PHTHALIC ANHYDRIDE

A dilute gaseous reaction mixture containing phthalic anhydride, such as may be obtained by the catalytic oxidation of naphthalene or *ortho*xylene, having the following composition by volume:—

Phthalic anhydride	-	-	-	1.1%
Oxygen	-	-	-	13.5
Carbon dioxide	-	-	-	3.0
Water	-	-	-	5.3
Nitrogen	-	-	-	75.9
Carbon monoxide	-	-	-	1.2

is passed through line 1 into absorber 2 wherein it is contacted with the dibutyl phthalate solvent introduced through line 3 or recycled through line 4. This absorber is a cylindrical tower of 7½ feet in diameter and 63 feet in height and contains 30 trays. If desired, the exit gases may be passed through a water scrubber to remove residual anhydride; e.g., a similar column with three trays (not shown in drawing). The gas flows upwardly through the absorber and the liquid flows downwardly therein, so that the scrubbing is carried out in a countercurrent manner. The temperature therein is maintained at 75° C. at the top and 115° C. at the bottom. The final scrubbed gas is substantially free of phthalic anhydride and is passed through line 5 to a discard system such as a stack.

The rich solvent liquor is passed from the absorber via line 6 through heat exchanger 7 wherein it is cooled somewhat and then passed via line 8 to column 9 wherein phthalic anhydride vapors are stripped therefrom and passed out via line 10. The vapors are passed therefrom via line 11 to condenser 12, wherein

they are liquefied, and then passed via line 13 to the product cooler, storage, or the like. Line 10 is connected directly to the vacuum system. A part of the condensate from condenser 12 is recycled via line 14 to the upper part of column 9.

The bottoms from column 9 are passed via line 15 to the upper part of column 16, wherein phthalic anhydride is stripped therefrom and removed via line 17, which line is connected directly to the vacuum system. Vapors are passed from line 17 via line 18 to condenser 19 wherein they are liquefied. Liquid is passed therefrom via line 20 to the lower part of column 9. A part of the liquid is recycled via line 21 to the upper part of column 16.

The bottoms from column 16 is the lean liquor or solvent which is substantially free from phthalic anhydride, and is passed via line 22 through heat exchanger 7 wherein it is cooled somewhat, and then via line 23 to cooler 24 wherein it is cooled, and then passed via line 4 to the upper part of absorber 2.

Column 9 is a cylindrical column 5 feet in diameter and 24 feet in height containing 10 trays. It is operated at a pressure of 33 mm. mercury at the top and a pressure of 55 mm. at the bottom; the corresponding temperatures being 172° C. at the top and 222° C. at the bottom. The stripping ratio therein is 0.46; i.e., the mols of rising vapor relative to the mols of downwardly flowing liquid.

Column 16 is a cylindrical column of 5 feet in diameter and 16 feet in height containing 5 trays. It is operated at a pressure of 23 mm. mercury at the top and a pressure of 40 mm. at the bottom; the corresponding temperatures being 193° C. at the top and 235° C. at the bottom. The stripping ratio therein is 0.46.

#### EXAMPLE 2. MALEIC ANHYDRIDE

The dilute gaseous reaction mixture containing maleic anhydride, such as may be obtained by the catalytic oxidation of benzene, having the following composition by volume:—

Maleic anhydride	-	-	-	0.7%
Oxygen	-	-	-	13.9
Carbon dioxide	-	-	-	2.4
Water	-	-	-	5.3
Nitrogen	-	-	-	75.3
Carbon monoxide	-	-	-	2.4

is processed as in Example 1, except that the temperature in the absorber 2 is maintained at 50–70° C., and the conditions in columns 9 and 16 are as follows:—

Column	9	16
Pressure		
Top	23 mm.	13 mm.
Bottom	45 mm.	25 mm.
Temperature		
Top	97° C.	85° C.
Bottom	115° C.	220° C.
Stripping ratio	0.46	0.46

In each of the foregoing examples, the

material throughputs are such that 1.1 to 1.8 parts by weight of product are recovered per 100 parts of scrubbing solvent, and the content of product in the feed gas is reduced to below 0.04%.

For phthalic anhydride recovery, the use of lower pressures such as in the range of 5 to 10 mm. in column 16 is undesirable since the corresponding temperatures are so low that the freezing point of phthalic anhydride may be encountered; and operation at such freezing point is impracticable.

For maleic anhydride recovery, the use of pressures in the range of 5 to 10 mm. in column 16 is undesirable, since to maintain a 5 mm. pressure drop across the column only

2 or 3 trays can be employed. However, the minimum number of trays for complete separation for maleic anhydride from dibutyl phthalate (that is, with infinity stripping ratio) is 4 trays. In comparable runs with fewer than 5 trays in column 16 and with a comparable throughput, the product loss in the exhaust gas is excessive due to the presence of product in the recycled scrubbing medium.

Comparable results to the foregoing examples are achieved with variations thereof as to equipment (tray columns or packed columns of equivalent separation efficiency) and conditions providing the operating conditions are maintained within the following ranges:—

Column	9	16
Number of trays - - - - -	10—20	5—10
Pressure		
Top - - - - -	10—35 mm.	13—25 mm.
Bottom - - - - -	40—60 mm.	20—60 mm.
Temperature		
Top - - - - -	75—175° C.	85—195° C.
Bottom - - - - -	110—225° C.	210—250° C.
Stripping ratio - - - - -	1.0—0.2	1.0—0.2

In separation efficiency, the number of trays indicated for column 9 is equivalent to 4 to 7.5 theoretical plates, and for column 16 the number of trays is equivalent to 2 to 4 theoretical plates. If a packed column is used as column 9, the height thereof should be equivalent to 4 to 7.5 theoretical plates; and if a packed column is used as column 16, the height thereof should be equivalent to 2 to 4 theoretical plates; such a column may be packed with Raschig rings, saddles, or the like. The correlation of actual trays with theoretical plates is made in accordance with known principles (see for instance *Trans. Am. Inst. Chem. Eng.*, August, 1946, pp. 741—755). The determination of the height equivalent to a theoretical plate for packed columns is made in accordance with known principles (see for instance *Perry, Chemical Engineer's Handbook*, 3rd Edition, McGraw-Hill, New York, 1950, pp. 618—621).

For phthalic anhydride recovery, the temperature in absorber 2 should be within the range of 70 to 120° C., e.g., 70 to 85° C. at the top and 110 to 120° C. at the bottom; and the relative flow rate of upwardly flowing gas relative to downwardly flowing liquid should be within the range of 20 to 40 mols of gas per mol of liquid.

For maleic anhydride recovery, the temperature in absorber 2 should be within the range of 40 to 80° C., and the relative flow rate of upwardly flowing gas relative to downwardly flowing liquid should be within the range of 40 to 60 mols of gas per mol of liquid.

Advantageous results are also obtained, although not necessarily all the advantages of the above described processes, if the first stripping operation is carried out in any suit-

able apparatus at a temperature in the range of 75 to 250° C. and an absolute pressure in the range of 10 to 150 mm. Hg., and the second stripping operation is carried out in analogous apparatus at a temperature in the range of 75 to 250° C. and an absolute pressure in the range of about 12 to 60 mm. Hg.

To separate a gaseous mixture containing both maleic anhydride and phthalic anhydride, two systems arranged in series may be used. The gas is first passed through an absorber arranged to absorb maleic anhydride (lower temperature conditions), and the absorbed maleic anhydride is then recovered. The gas is then passed to a second absorber arranged to absorb phthalic anhydride (higher temperature conditions), and the absorbed phthalic anhydride is then recovered. Alternatively, using a single system, the gaseous mixture may be processed first to recover maleic anhydride, and then reprocessed to recover phthalic anhydride, using the indicated conditions in each case.

If the initial feed gas contains substantially more than about 2% by volume of desired product, it is advantageous to cool the gas to a temperature below the condensation point of the anhydride, to liquefy a portion thereof, and then remove it; in other words, to fractionally condense out a part of the product therein so as to leave a feed gas containing not more than about 2% by volume of the desired product.

Variations and modifications of the invention will be apparent to one skilled in the art in view of the foregoing disclosures, and it is intended to include within the invention all such variations and modifications except as do not come within the scope of the appended claims.

What we claim is:—

1. A process for the recovery of only maleic anhydride or only phthalic anhydride from a dilute gaseous mixture containing maleic anhydride or phthalic anhydride respectively, or containing a mixture of both of the said anhydrides, which process comprises scrubbing only the maleic or only the phthalic anhydride vapor from the gaseous mixture with dibutyl phthalate as scrubbing liquor, stripping the absorbed anhydride from the resulting solution comprising only one of the said anhydrides at a temperature in the range of 75 to 250° C. and an absolute pressure in the range of 10 to 150 mm. Hg. and then subjecting the partially stripped solution to further stripping under more severe conditions at a temperature in the range of about 75 to 250° C., and an absolute pressure in the range of about 12 to 60 mm. Hg., recycling the anhydride product from the second stripping operation to the first stripping operation, and recycling the stripped solvent from the second stripping operation to the anhydride absorption step.
2. A process according to Claim 1 wherein the lean solvent returned to the anhydride absorption step is passed in indirect heat exchange relation to the anhydride enriched solvent passing from the absorption step to the first stripping operation.
3. Process according to Claim 2, wherein the gaseous mixture is cooled to a temperature below the condensation point of the anhydride to liquefy and separate a portion of said anhydride prior to the absorption step.
4. Phthalic anhydride whenever obtained by a process as set forth in any of the preceding claims.
5. Maleic anhydride when ever obtained by a process as set forth in any of Claims 1—3.

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1 SHEET

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This drawing is a reproduction of the Original on a reduced scale.

